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6. AUTHORS

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14. ABSTRACT

Under MURI support, we are 1) demonstrating the formation of highly functional 3-D photonic crystals using interference lithography; the breakthrough tools are be gray-scale phase masks designed with genetic algorithms (GAs) and fabricated through scanning probe imprint lithography; 2) fabricating electrically active single crystal III-V heterostructured 3-D photonic crystals; 3) demonstrating the holographic patterning of 3-D photonic crystals in IR transparent chalcogenide glasses; 4) developing a new class of ultrafast charge and discharge battery systems.

15. SUBJECT TERMS

ceramics, self-assembly, materials science and engineering, photonic materials, colloids, holography, sol-gel

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
UU	UU	UU	UU		Paul Braun
					19b. TELEPHONE NUMBER 217-244-7293

Report Title

Self-Assembly of 3-D Multifunctional Ceramic Composites for Photonics and Sensors

ABSTRACT

Under MURI support, we are 1) demonstrating the formation of highly functional 3-D photonic crystals using interference lithography; the breakthrough tools are be gray-scale phase masks designed with genetic algorithms (GAs) and fabricated through scanning probe imprint lithography; 2) fabricating electrically active single crystal III-V heterostructured 3-D photonic crystals; 3) demonstrating the holographic patterning of 3-D photonic crystals in IR transparent chalcogenide glasses; 4) developing a new class of ultrafast charge and discharge battery systems. Each of these specific aims builds directly off discoveries supported by our earlier MURI work. Specific applications include new IR photonic crystal based filters for multispectral imaging, optical metamaterials, and GaAs based 3-D photonic crystal lasers.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

A. Brzezinski, Y.-C. Chen, P. Wiltzius and P. V. Braun: Complex three-dimensional conformal surfaces formed by atomic layer deposition: Computation and experimental verification, Journal of Materials Chemistry, 19, 9126-9130 (2009).

J. Shin, J.-T. Shen and S. Fan: Three-Dimensional Metamaterials with an Ultrahigh Effective Refractive Index over a Broad Bandwidth, Physical Review Letters, 102, 093903 (2009). DOI: 10.1103/PhysRevLett.102.093903

K. A. Arpin, A. Mihi, H. T. Johnson, A. J. Baca, J. A. Rogers, J. A. Lewis and P. V. Braun: Multidimensional Architectures for Functional Optical Devices, Advanced Materials, 22, 1084-1101 (2010). (cover feature)

J. Shin, J.-T. Shen and S. Fan: Transmission Through a Scalar Wave Three-Dimensional Electromagnetic Metamaterial and the Implication for Polarization Control, Journal of Nanoscience and Nanotechnology, 10, 1737-1740 (2010). DOI: 10.1166/jnn.2010.2036.

H. Zhang, X. Yu and P.V. Braun: Three-dimensional bicontinuous ultrafast-charge and -discharge bulk battery electrodes, Nature Nanotechnology (2011). DOI: 10.1038/nnano.2011.38

Number of Papers published in peer-reviewed journals: 5.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

P.V. Braun, “3D Composite Structures for Storing, Generating, and Harvesting Photons and Electrons,” 11th International Conference on Advanced Materials, Rio de Janeiro, Brazil, September 2009.

P.V. Braun, (Plenary) "Self-Assembly of Functional Composites for Storing, Generating and Harvesting Photons and Electrons" Composites at Lake Louise, Banff, Alberta, Canada, October 2009.

P.V. Braun, “3D Photonic Crystals with Embedded Dielectric, Metallic and Emissive Features for Controlling the Generation and Harvesting of Photons”, META ’10, Cairo, Egypt, February 2010.

P.V. Braun, “Self-Assembly of 3D Nanostructured Electrodes for Ultrafast Charge and Discharge Li-Ion and NiMH Batteries”, American Chemical Society, San Francisco, CA, March 2010.

P.V. Braun, “Holographic Patterning of 3D Optoelectronically Active Photonic Crystals”, E-MRS, Strasbourg, France, June 2010.

P.V. Braun, “Combining Top-down and Bottom-Up Assembly for Energy Storage and Harvesting”, Workshop on Colloids and Interface: Microstructured Fluids and Materials, KAIST, Seoul, Korea, August 2010.

Number of Presentations: 6.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Gardner, A., S. Gupta, P.V. Braun, and W.P. King, "Nanoindent Nanoimprint Lithography for the Fabrication of 3D Photonic Crystals," Proceedings of the Nanoprint and Nanoimprint Conference, Copenhagen, Denmark, October 2010.

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 1

Peer-Reviewed Conference Proceeding publications (other than abstracts):

P.V. Braun, "Direct Laser Writing of Photoresponsive Colloids for Microscale Patterning of 3D Porous Structures," SPIE Photonics West, January 2010 (submitted to: Laser Applications in Microelectronic and Optoelectronic Manufacturing XV",

P.V. Braun, "Templated Growth of and Optical Emission from Single Crystal GaAs 3D Photonic Crystals," SPIE Photonics West, January 2010 (submitted to Advanced Fabrication Technologies for Micro/Nano Optics and Photonics III),

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 2

(d) Manuscripts

Number of Manuscripts: 0.00

Patents Submitted

Patents Awarded

Awards

Friedrich Wilhelm Bessel Research Award, Alexander Humboldt Foundation, 2010 (P. V. Braun)

Stanley H. Pierce Faculty Award, College of Engineering, UIUC, 2010 (P. V. Braun)

Graduate Students

NAME	PERCENT_SUPPORTED
Andrew Gardner	1.00
Erik Nelson	0.50
Aaron Jackson	0.50
Dara Gough	0.50
Jonathan Lange	0.50
Ian Blitz	0.25
FTE Equivalent:	**3.25**
Total Number:	**6**

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Matthew George	1.00
Yoonho Jun	1.00
Masao Miyake	1.00
Mark Losego	0.50
FTE Equivalent:	**3.50**
Total Number:	**4**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
William King	0.05	No
FTE Equivalent:	**0.05**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME	
Asfand Waqar	
Total Number:	**1**

Names of personnel receiving PHDs

NAME	
Andrew Brzizinski	
John Busbee	
Xindi Yu	
Erik Nelson	
Abigail Juhl	
Dara Gough	
Total Number:	**6**

Names of other research staff

NAME	PERCENT_SUPPORTED	
Erica Malloch	0.08	No
FTE Equivalent:	**0.08**	
Total Number:	**1**	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

Final Report
April 2011

MURI: "Self-Assembly of 3-D Multifunctional Ceramic Composites for Photonics and Sensors"
Grant number: DAAD19-03-1-0227.
PI: Paul Braun, University of Illinois at Urbana-Champaign

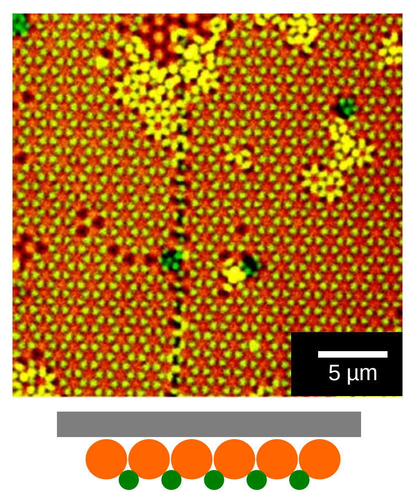
The stated goals of this MURI, as contained within the initial proposal were:
We aim to create: 1) new colloidal self-assembly routes that combine nanoparticle- and DNA-mediated colloidal assembly with colloidal epitaxy to create colloidal crystals with exact orientation with respect to a substrate and defined crystal symmetries; 2) multibeam ceramic holography as a route to 3-D nano- and microscale periodic ceramics; 3) ceramic/liquid crystal composite optical switches; 4) UV and multiphoton patterning of sol-gel ceramic precursors as a route to sub micron engineered ceramic structures; and 5) robotically controlled deposition of ceramic nanoparticle-polymer composites.

The stated goals of the MURI expansion funding were:
We aim to 1) demonstrate the formation of highly functional 3-D photonic crystals using interference lithography; the breakthrough tools will be gray-scale phase masks designed with genetic algorithms (GAs) and fabricated through scanning probe imprint lithography; 2) fabricate electrically active single crystal III-V heterostructured 3-D photonic crystals; 3) demonstrate the holographic patterning of 3-D photonic crystals in IR transparent chalcogenide glasses.

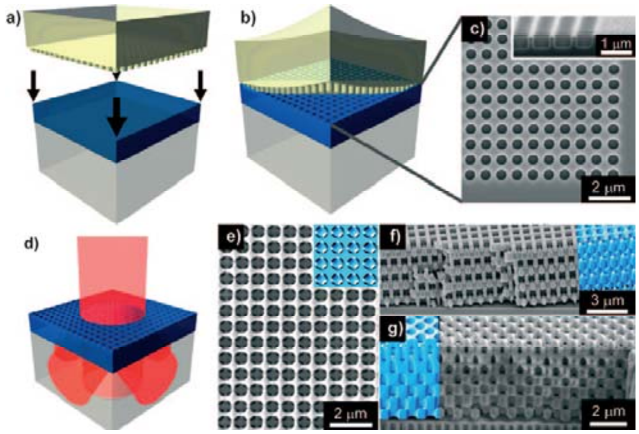
We are quite pleased to report that we succeeded in the vast majority of the stated goals. In addition, a number of quite significant unanticipated discoveries resulted from this work. The successes will be illustrated with selected figures and brief textual descriptions.

Initial Proposal Goals:
1) New colloidal self-assembly routes that combine nanoparticle- and DNA-mediated colloidal assembly with colloidal epitaxy to create colloidal crystals with exact orientation with respect to a substrate and defined crystal symmetries.

We demonstrated a means to adapt DNA ligation to DNA-mediated colloidal assembly to form non-face centered cubic structures, representing a new paradigm for colloidal assembly. Due to the sequence specificity of DNA ligase activity, i.e. only a perfectly hybridized duplex may be ligated; non-ligated sequences are available for subsequent assembly. This aspect of DNA ligase provides a route towards hierarchical assembly of colloidal structures. DNA ligation provides enormous advantages for self-assembly: once ligated, DNA assembled structures are permanent, assembly is sequence specific; the assembly process is non-destructive to unhybridized DNA; and ligation conditions are compatible with standard self-assembly conditions. Our first work on DNA driven colloidal assembly was published by Braun, Lu, Wiltzius, et al. in JACS 2008 and the ligation manuscript is in preparation.



2) Multibeam ceramic holography as a route to 3-D nano- and microscale periodic ceramics.

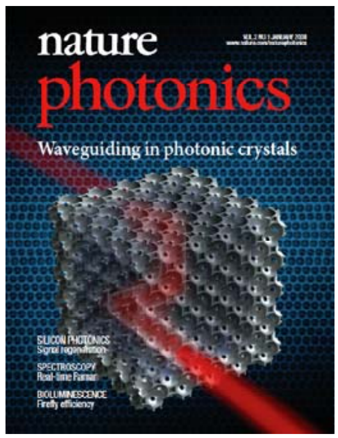


We reported for the first time a silsesquioxane-based photoresist that is compatible with 3D interference lithography and offers many of the same advantages of organic photoresists, including sub-micrometer resolution, but with material properties more amenable to post-fabrication processing, such as improved thermal stability and resistance to reactive-ion etching. The photoresist is based on the acidcatalyzed cross-linking of poly(methylsilsesquioxane) (PMSSQ). The figure illustrates the maskless PnP process for the fabrication of 3D periodic microstructures. a), b) Schematic views of the micromolding process using an elastomeric PDMS stamp. c) Plan-view SEM image and cleaved cross-section (inset) of the micromolded PMSSQ photoresist surface relief structure. d) Exposure through the relief structure generates diffracted beams for maskless PnP, which upon post-baking and development generates 3D periodic PMSSQ microstructures. SEM images of e) plan view, f) {100} cleaved section, g) focused ion beam milled cross-section (ca. {110}). The blue insets represent modeling of the structure on the basis of a threshold approximation of the intensity-squared distribution assuming circularly polarized, 800 nm exposure wavelength, and the following imprint design: 760 nm pitch square array of cylindrical holes with 305 nm radius and 400 nm relief depth (Braun et al., Angew. Chem. 2009).

3) Ceramic/liquid crystal composite optical switches.

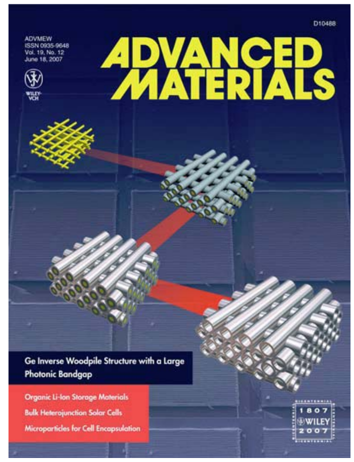
Preliminary work was performed in this direction by Wiltzius, indicating optical switching was possible. However the strength of the optical modulation was small relative to known methods for optical switching, and thus the team decided to focus their efforts in other directions.

4) UV and multiphoton patterning of sol-gel ceramic precursors as a route to sub micron engineered ceramic structures.



The system used in point 2 above was a multiphoton sensitive sol-gel ceramic precursor. Through various materials transformation strategies, including ceramic deposition strategies, Braun and co-workers formed a 3D optical waveguide in a silicon photonic band gap material. High-resolution three-dimensional features are first formed within a silica colloidal crystal by means of two-photon polymerization, followed by a high-index replication step and removal of the opal template to yield embedded defects in three-dimensional silicon photonic crystals. We demonstrated the coupling of bandgap frequencies to resonant modes in planar optical cavities and the first waveguiding of near-infrared light around sharp bends in a complete-photonic-bandgap material (Braun et al., Nature Photonics 2008).

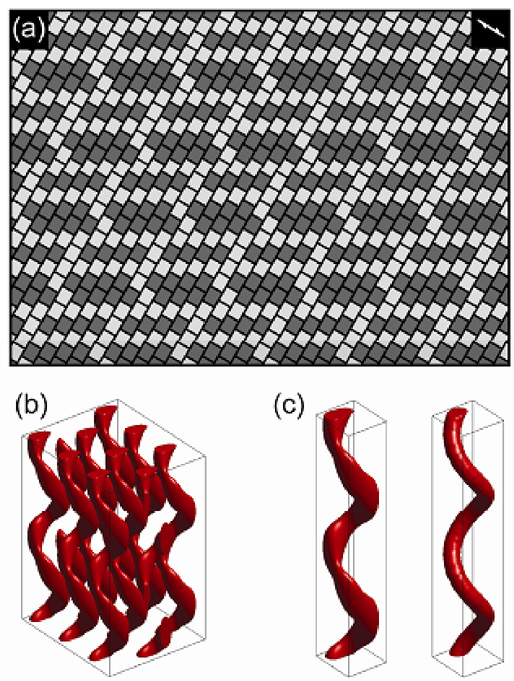
5) Robotically controlled deposition of ceramic nanoparticle-polymer composites.



The team was very active in this area, and multiple publications resulted from this work. Through a close coupling of theory, simulation, and experiment, the team was able to fabricate 3D ceramic and semiconductor structures with large complete photonic bandgaps. Realization of such structures has been an important goal since the concept of a PBG was introduced two decades ago. Many proposed structures exhibit PBGs with theoretical relative widths below 5%, often too narrow for application, since structural inhomogeneties may reduce the size, or even close, PBGs by introducing unwanted modes into the band structure. We reported the simulation, assembly, and optical properties of both Si and Ge inverse woodpile structure with very wide PBGs (15-25%). These structures were created by direct-write assembly of a polymeric template followed by sequential deposition of oxides and Si or Ge. The photonic response is maximized by tuning the semiconductor filling fraction in accordance with theoretical predictions. Upon removal of any sacrificial layers, the reflectance spectra acquired from the structures show large reflectance peaks in the mid-IR indicative of PBGs (Braun, Fan, Lewis, et al., Adv. Mater. 2006 and 2007).

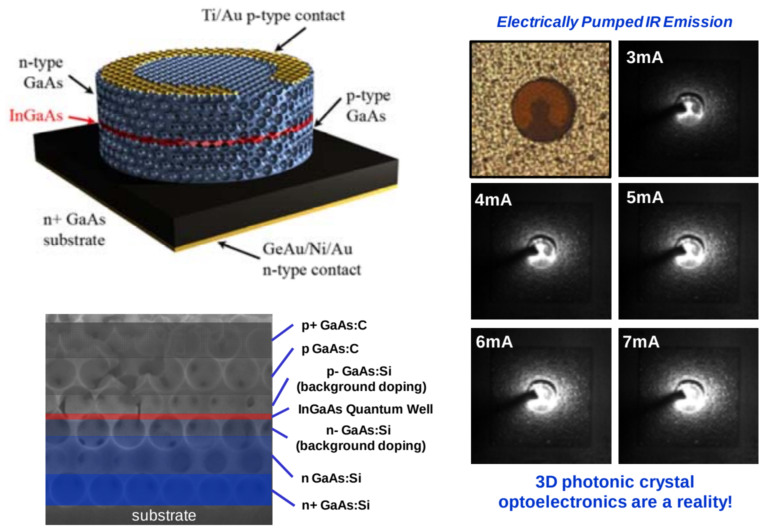
Expansion Phase:

1) Demonstration of the formation of highly functional 3-D photonic crystals using interference lithography; the breakthrough tools were be gray-scale phase masks designed with genetic algorithms (GAs) and fabricated through scanning probe imprint lithography



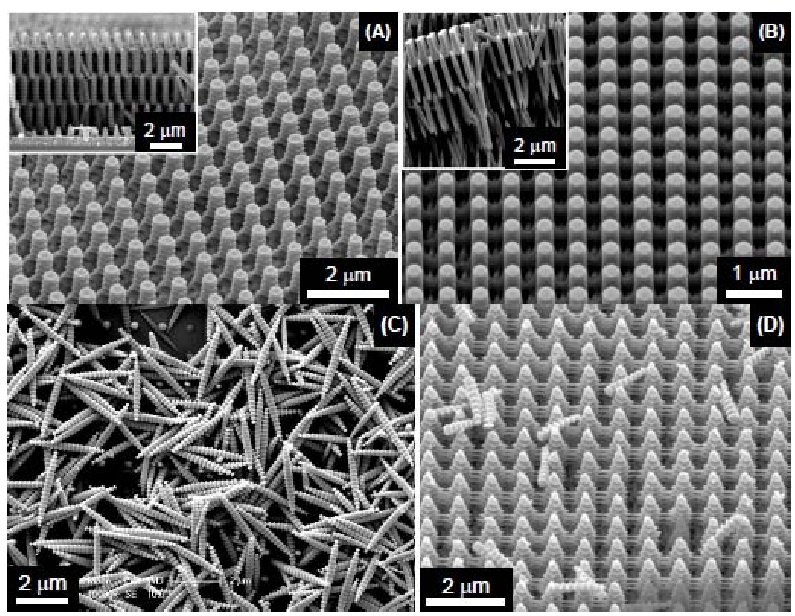
Our work in this area was detailed in the 2010 MURI annual report. Since that report, we have continued to advance the fabrication and modeling capabilities of the team. We have now demonstrated theoretically, and in some cases experimentally that interference lithography, coupled with nano-indentation fabrication methods allow for the fabrication of previously unrealizable 3D structures. Structures demonstrated include broadband circular polarizers that are responsive in the near-IR and 3D structures with controlled defects. The figure shows (a) optimized grating profile and incident polarization (upper right inset) for direct helical structures. Light grey pixels are raised and dark grey pixels are recessed. Part (b) depicts multiple repeat units of the resultant structure, illustrating its hexagonal periodicity. Part (c) illustrates the side-by-side comparison between two repeat units of the resultant structure and the two repeat units of the target. Braun, Fan, King, Wiltzius, et al., manuscript in preparation.

2) Fabrication of electrically active single crystal III-V heterostructured 3-D photonic crystals



Optoelectronic devices have long benefited from structuring in multiple dimensions on microscopic length scales. Preserving crystal epitaxy, a general necessity for good optoelectronic properties, while imparting a complex three-dimensional structure remains, however, a significant challenge. Three-dimensional (3D) photonic crystals are one class of materials where epitaxy of 3D structures would enable new functionalities. Many 3D photonic crystal devices have been proposed, including zero-threshold lasers, low-loss waveguides, high efficiency LEDs and solar cells, but have generally not been realized due to materials limitations. Exciting concepts in metamaterials, including negative refraction and cloaking, could be made practical using 3D structures which incorporate electrically pumped gain elements to balance the inherent optical loss of such devices. Here we demonstrate the 3D-template-directed epitaxy of III-V materials which enables formation of 3D structured optoelectronic devices. We illustrate the power of this technique by fabricating an electrically-driven 3D photonic crystal LED. Braun, Wiltzius et al., manuscript under review.

3) Demonstration of the holographic patterning of 3-D photonic crystals in IR transparent chalcogenide glasses.



Inorganic photoresists that can be directly patterned in three dimensions via 3D interference lithography based fabrication approaches are attractive materials for the fabrication of complex microfluidic and micro-optical components such as chaotic mixing elements or 3D photonic crystals. Several chalcogenide glass based photoresist systems based on amorphous semiconductors from the As-S-Se ternary system have been developed or adapted for these purposes. The 3D structures shown in the figures here were formed using holographic exposure of As_2Te_3-based chalcogenide glasses. The structures formed using this system have a high index of refraction and strongly non-linear optical properties, making them attractive candidates for engineered photonic crystal based devices (Braun, King, Wiltzius, et al., manuscript in preparation).